Overview of Mercury Cycle

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Introduction

The fish in Minnesota lakes and streams are contaminated by unacceptable levels of mercury, virtually all of which is delivered by the atmosphere.

Where does this atmospheric mercury come from?

What proportion is from Minnesota sources?

How does mercury get into fish?

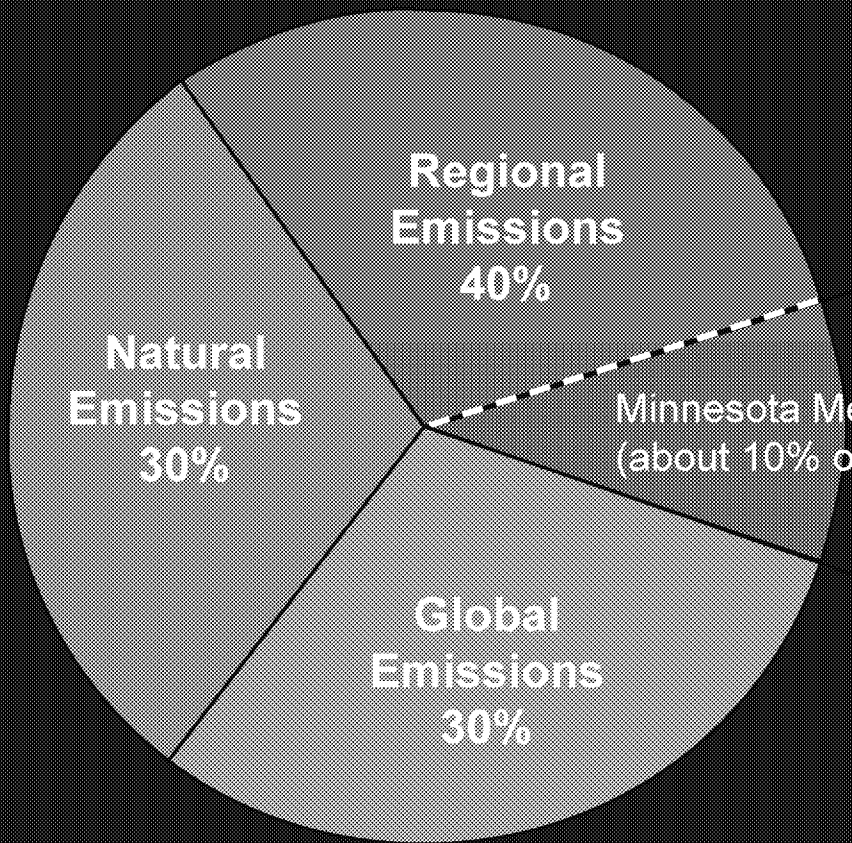
How can the effect of mercury emissions on fish contamination be modeled?

Globally, about 70% of mercury in the atmosphere Is anthropogenic (metric tons emitted per year)

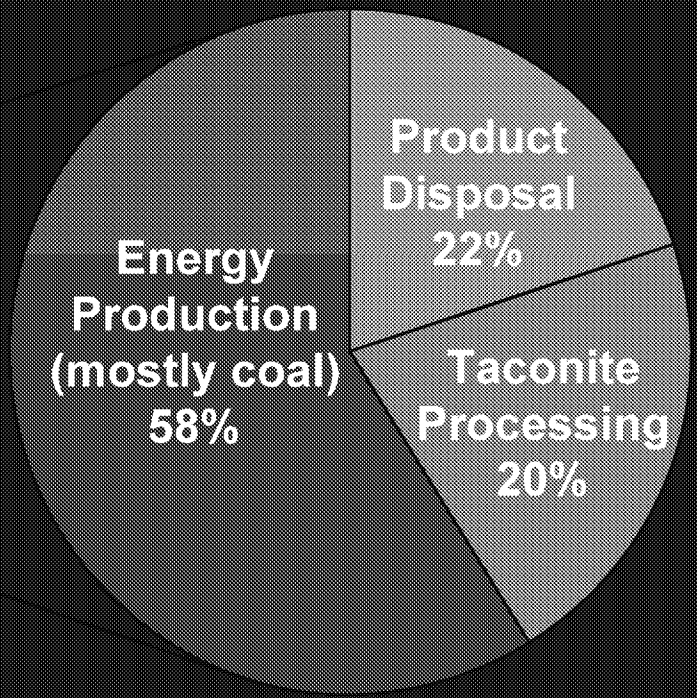
Source	Seigneur et al. 2004	Bergan et al. 1999	Mason & Sheu 2002
Direct Anthropogenic	2,143	2,160	2,400
Recycled Anthropogenic	2,134	2,000	2,090
Total anthropogenic	4,277	4,160	4,490
Natural	2,134	1,900	2,110
Total (% of Anthropogenic Origin)	6,411 (67%)	6,060 (69%)	6,600 (68%)

Most scientists agree on the total input of mercury to the atmosphere and the relative amount of this mercury that has come from anthropogenic sources.

MPCA estimated in 2005 that Minnesota Hg emissions accounted for 10% of Hg deposition in Minnesota



Source of Hg deposited in MN



Minnesota Hg emissions in 2005

Three important forms of mercury

Elemental mercury: Hg(0)

Divalent, or oxidized, mercury: Hg(II)

Methylmercury: CH_3Hg^+, or MeHg

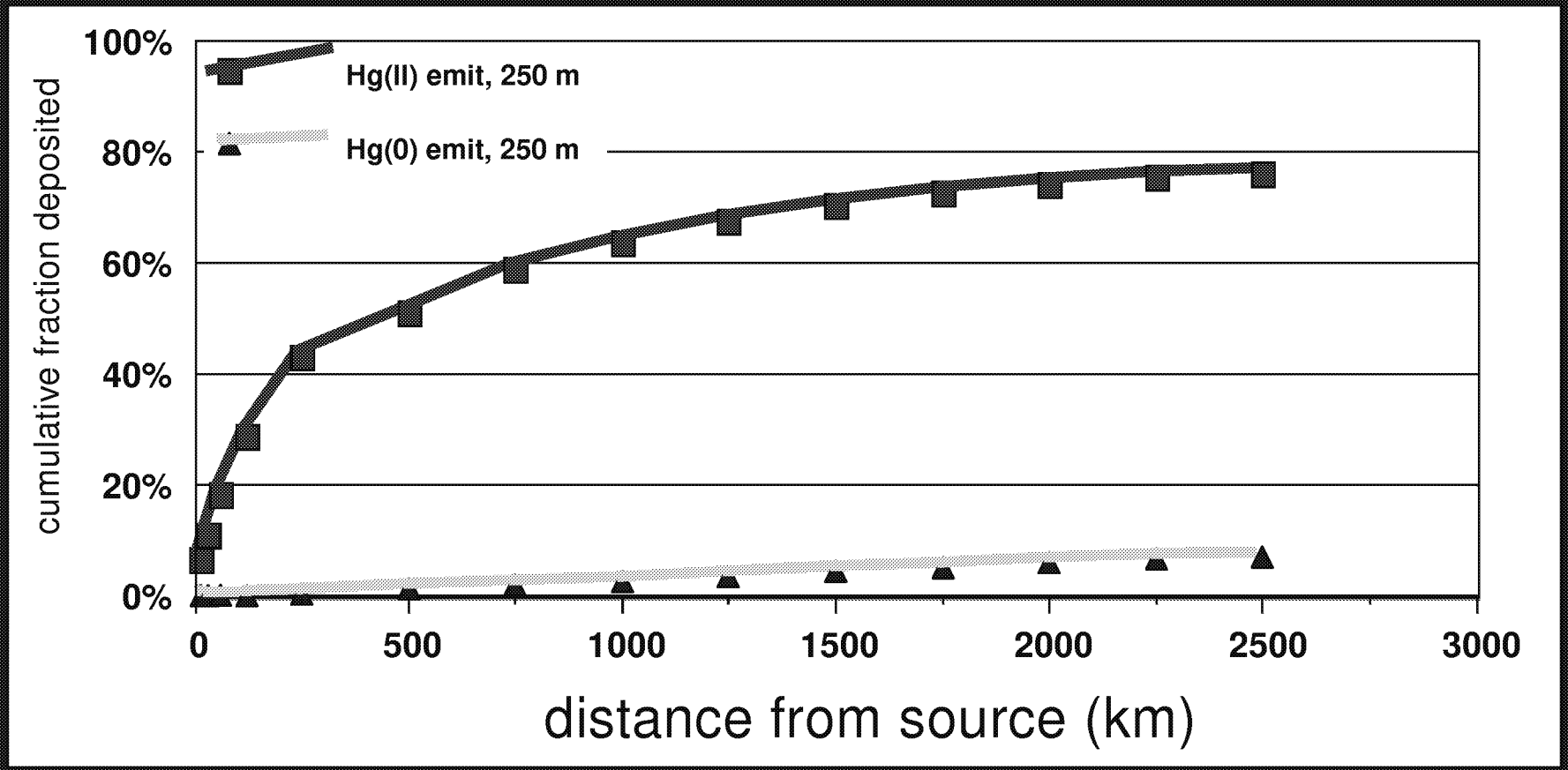
Elemental Mercury: Hg(0)

- Dominant form in atmosphere, and in most air emission sources.
- This is the vapor when liquid mercury evaporates.
- Toxic at high (>300 ng/m^3) air concentrations because it is absorbed by the lungs (spilled Hg is hazardous indoors). Outdoor air < 2 ng/m^3.
- Not water soluble and relatively inert. Therefore, subject to long-distance atmospheric transport.

Divalent, or oxidized: Hg(II)

- Water soluble.
- Usually less than 1% of Hg(0) in the atmosphere, probably present as mercuric chloride ($HgCl_2$) .
- Dominant form in rainfall, water, sediments, soil, some emission sources (notably uncontrolled incinerators because of chlorine in plastics).
- In vapor phase, tends to stick to surfaces, such as foliage.

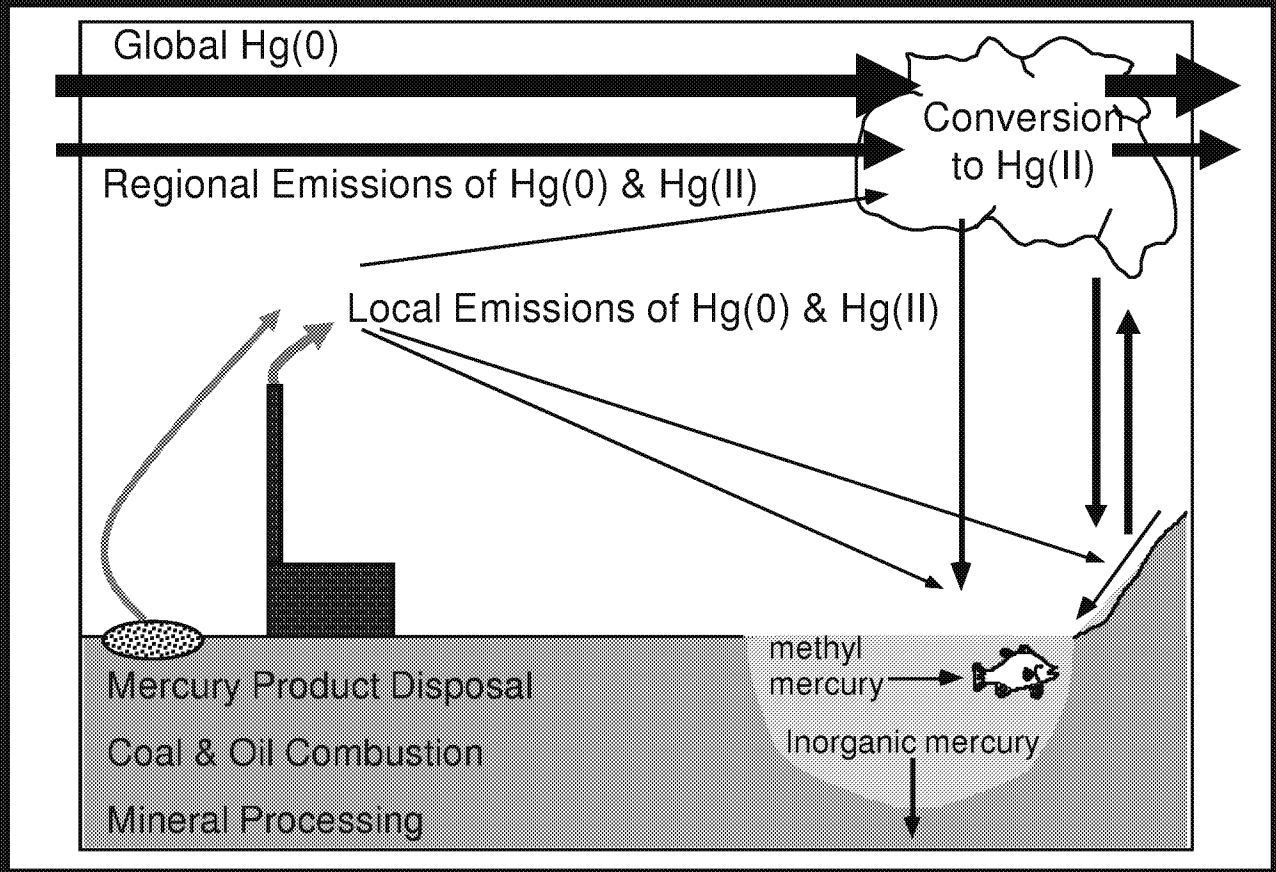
Hg(II) is deposited faster than Hg(0), but still slowly (50% within 500 km when emitted at high elevation)

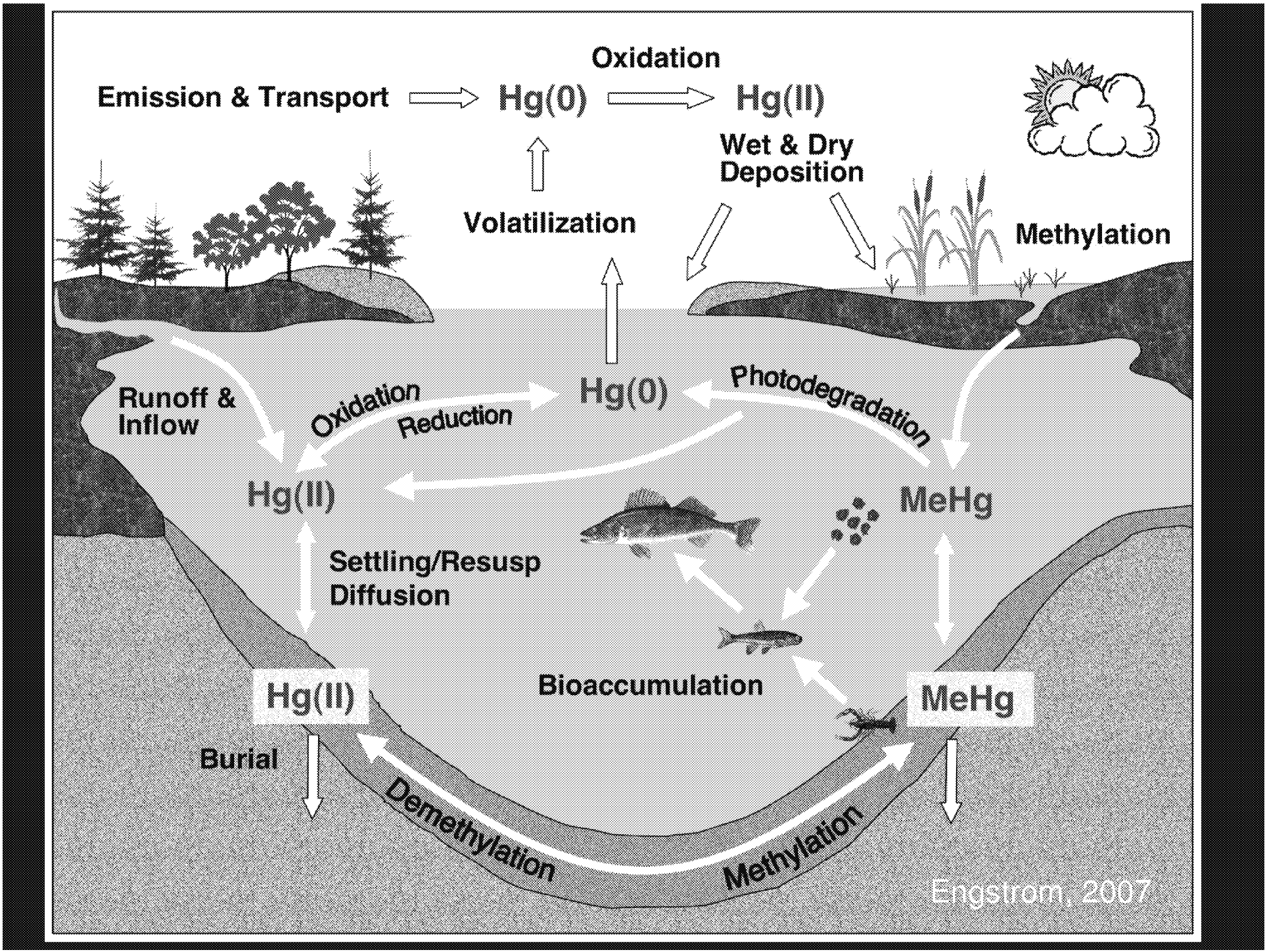


From Mark Cohen, 2004 (NOAA)

http://www.arl.noaa.gov/data/web/reports/cohen/26_USGS_source_apportionment_talk.pdf

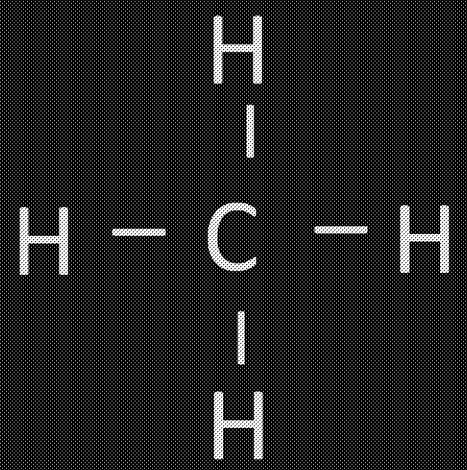
Delivery of atmospheric mercury to lakes & rivers



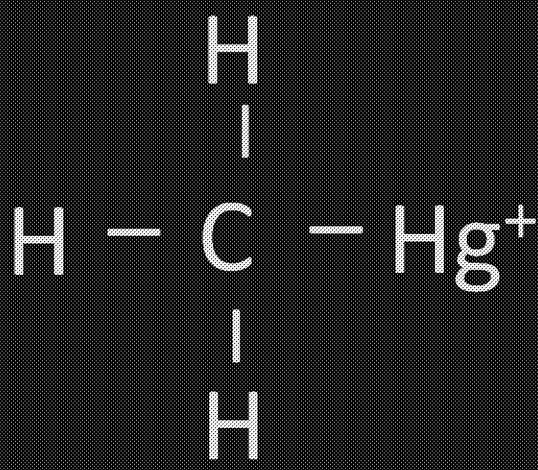

Oxidation
Emission & Transport
Hg(0)
Hg(II)
Wet & Dry Deposition
Volatilization
Methylation
Runoff & Inflow
Oxidation
Reduction
Hg(0)
Photodegradation
Hg(II)
MeHg
Settling/Resusp
Diffusion
Hg(II)
Bioaccumulation
MeHg
Burial
Demethylation
Methylation
Engstrom, 2007

Methylmercury: CH_3Hg^+, or MeHg

- The form of mercury that concentrates in fish.
- Simple organic compound.
- Behaves much differently than inorganic mercury.
- Chemical formula CH_3Hg^+, sometimes just MeHg.
- Accumulates in proteins (e.g. muscle), unlike many contaminants that accumulate in fat.

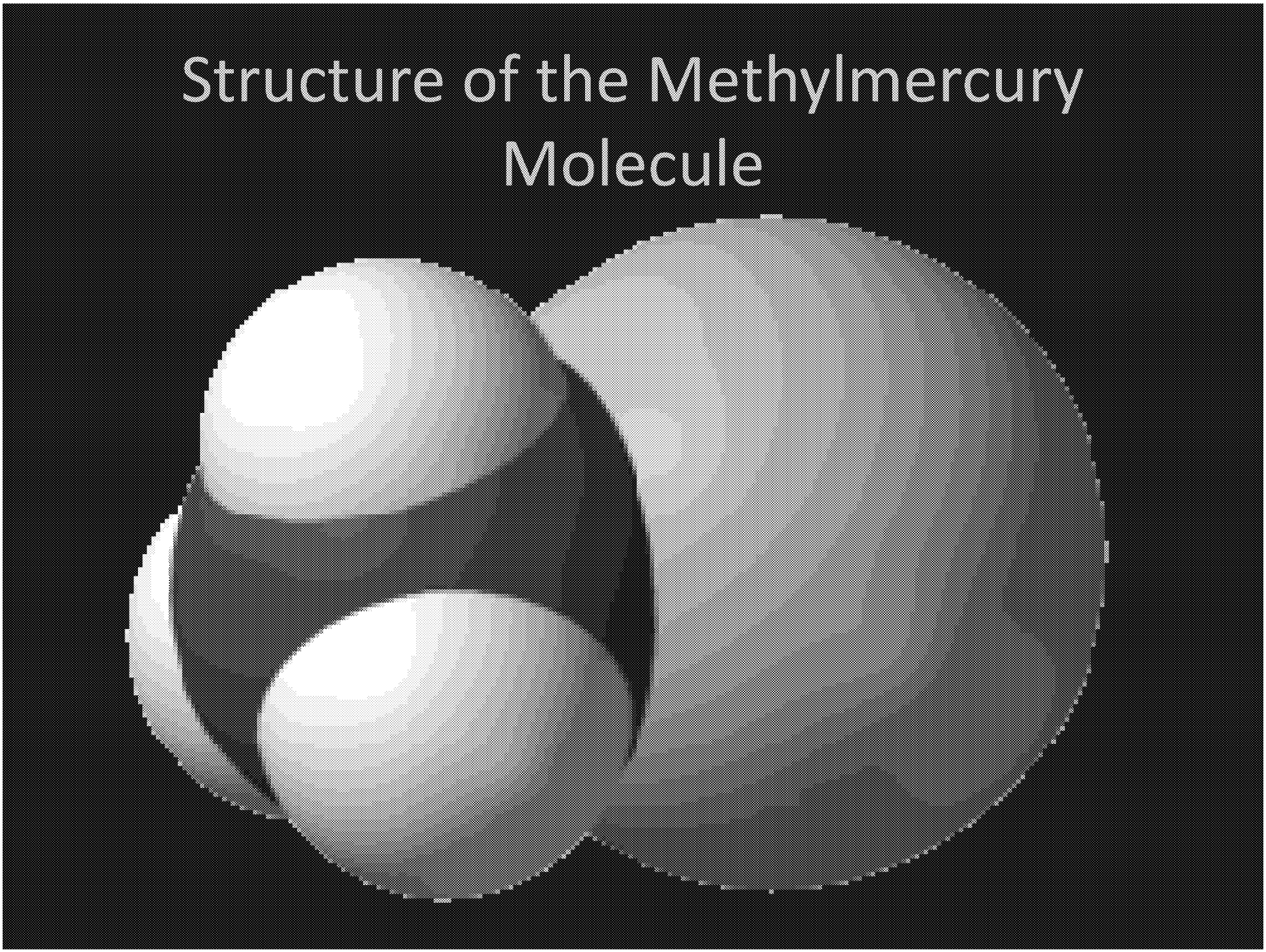


methane



methylmercury

Structure of the Methylmercury Molecule

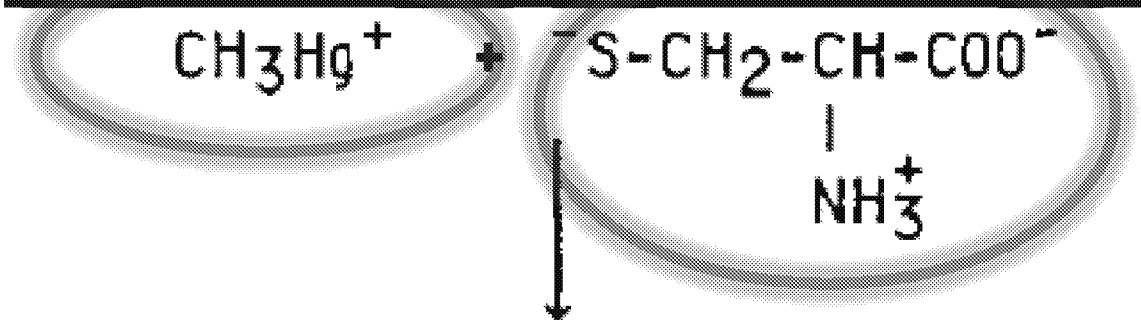


One important fact

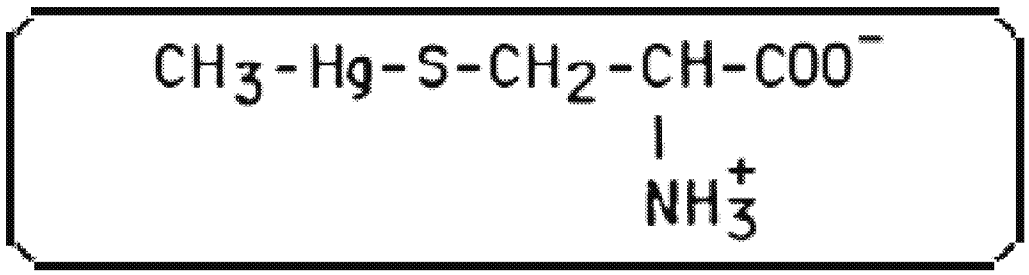
Mercury can form very strong bonds with sulfur.

For instance, cinnabar – HgS

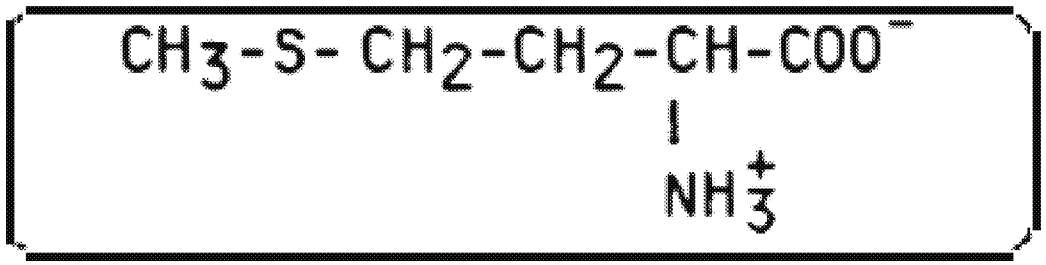
The MeHg-Cysteine complex may mimic methionine, and so is built into protein



CYSTEINE



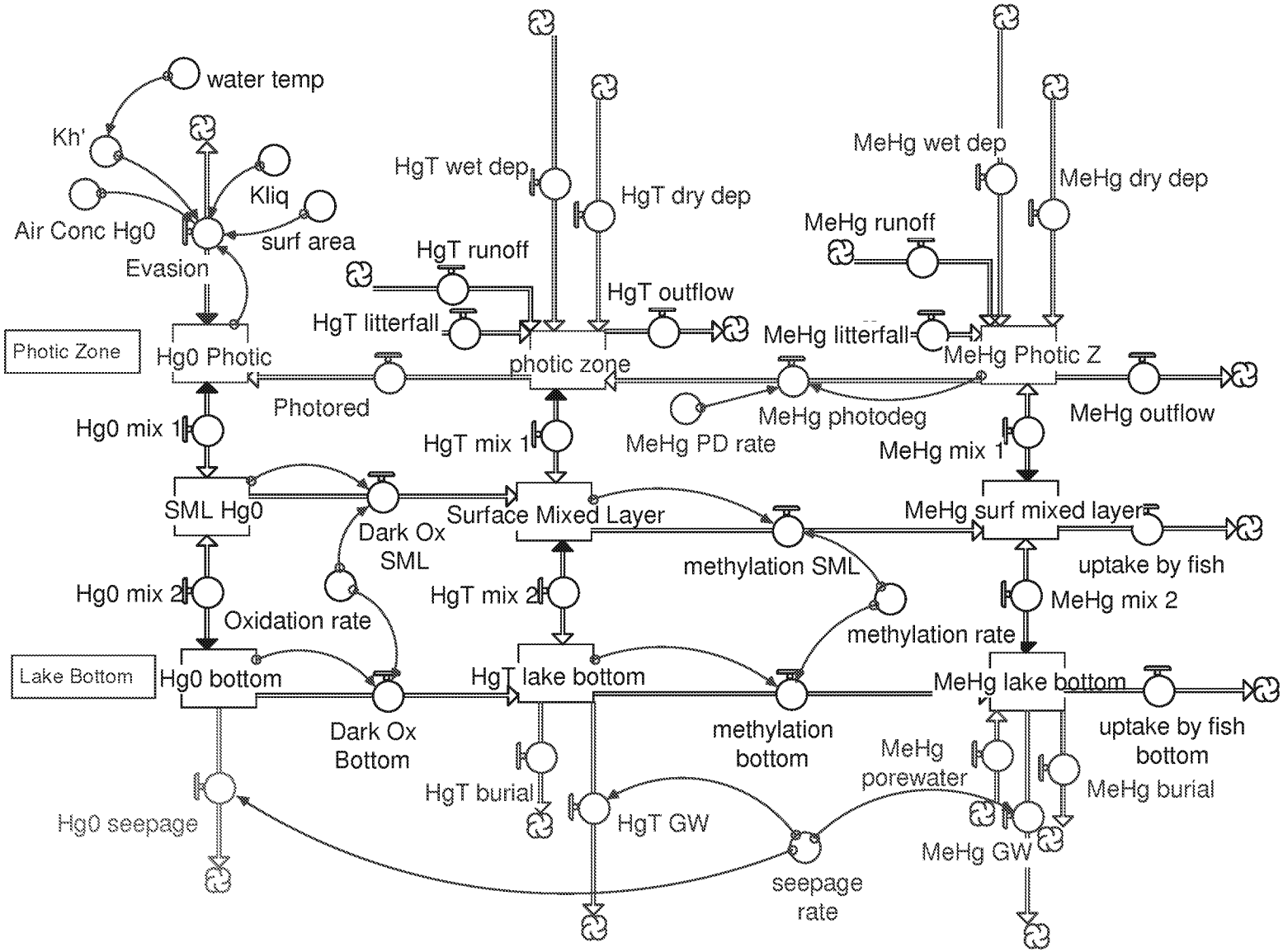
METHYLMERCURY (COMPLEX)



METHIONINE

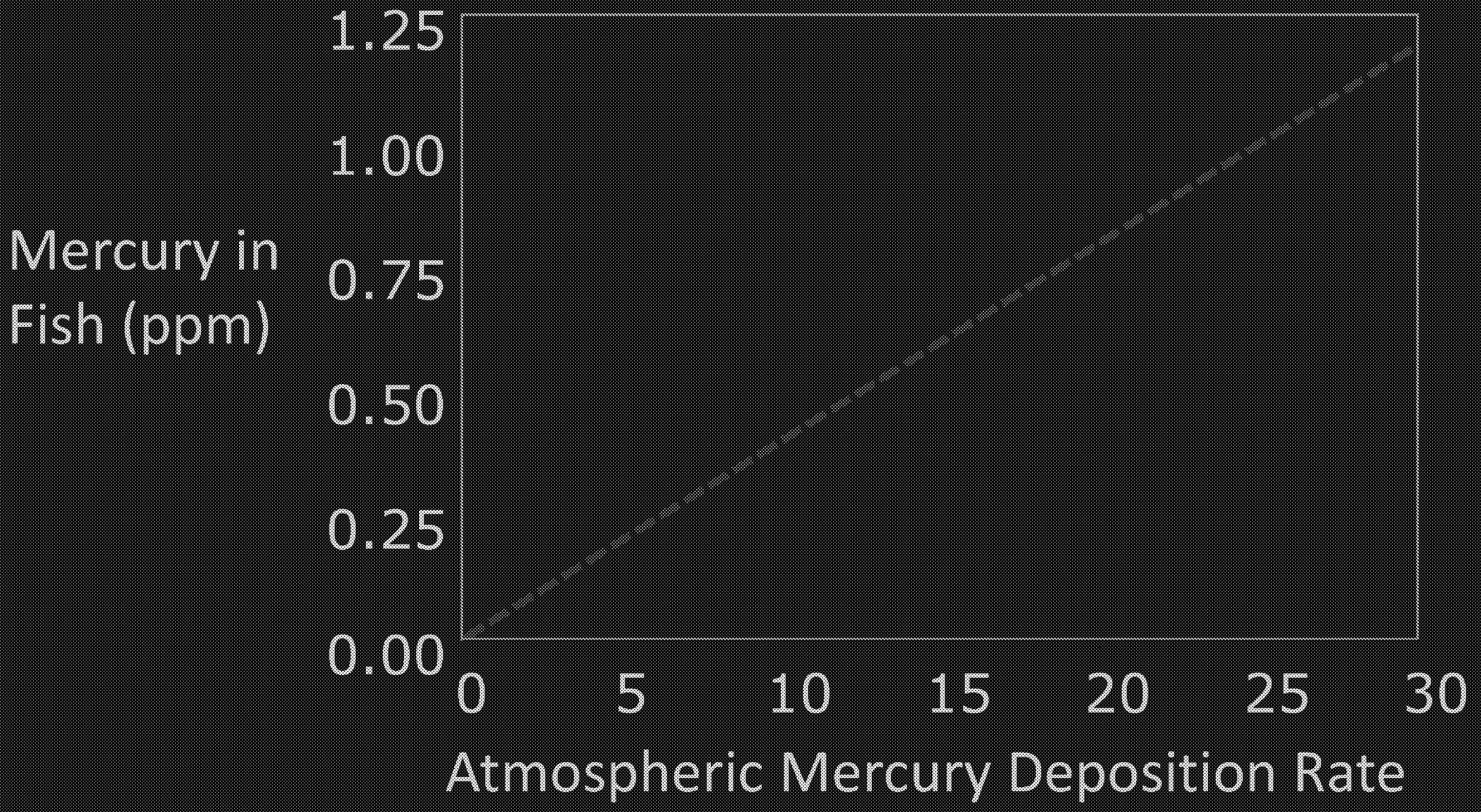
Clarkson (1993)

Problem: Mechanistic models of Hg methylation and bioaccumulation are more complicated than our current scientific understanding

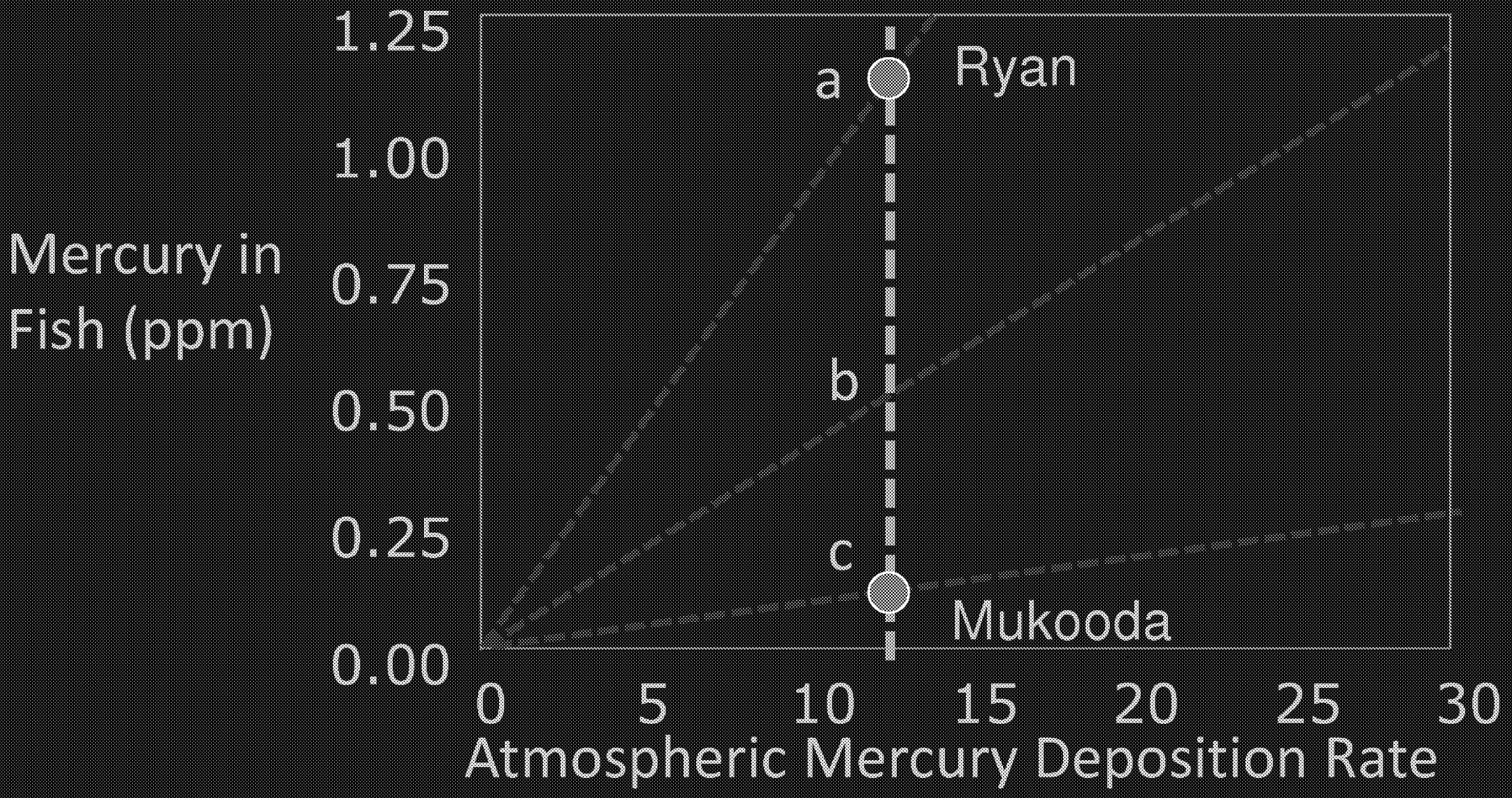


Hines Ph.D. Thesis, 2004

Computer Models Predict that Hg in Fish is Proportional to Hg Deposition



But lakes differ in the efficiency that atmospheric Hg accumulates in fish

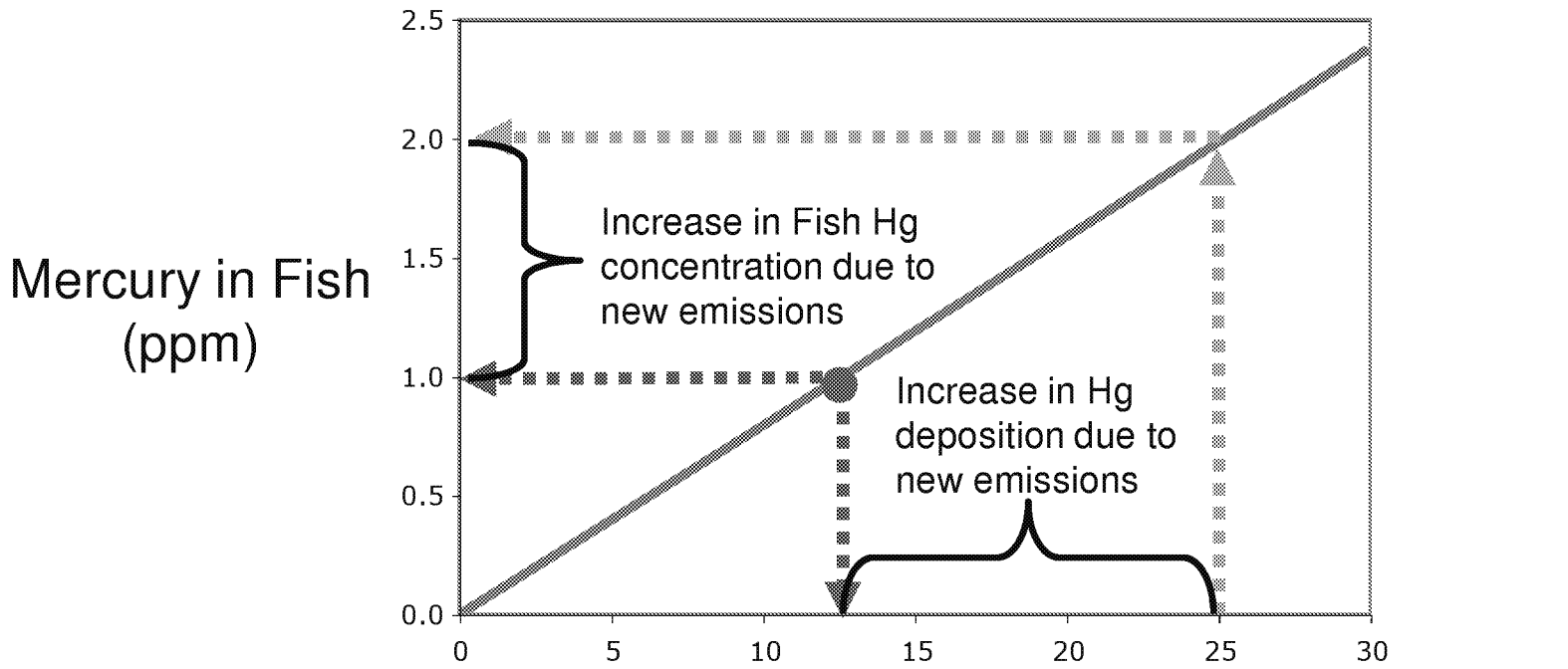


Wiener et al. 2006. Environmental Science & Technology.

All things being equal:
Mercury in fish *in a given lake* will be proportional to the load from atmospheric deposition of mercury.

- What are "all things"?
  - Methylation efficiency in the lake and its watershed.
  - Length of the food chain.
  - Export of Hg and MeHg from the watershed….
- EPA ran several mechanistic models to steady state, supporting the assumption of proportionality.
- For new facilities, MPCA models atmospheric deposition and export from the watershed.
  - Change in fish is proportional to % change in loading.
  - Bigger watersheds are less sensitive to changes in local emissions.
- Instead of a mechanistic model, MPCA uses proportionality to calculate changes in fish contamination.
- US EPA Science Advisory Board recently (2012) affirmed the the use of proportionality in modeling.

Proportionality predicts the effect of an increase (or decrease) in atmospheric Hg deposition



12.5 µg/m² yr is ambient Hg deposition

Questions?